Balloon-Borne Observations of Mid–Latitude Hydrofluoric Acid

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Measurements of HF in the lower stratosphere have been made by the Jet Propulsion Laboratory MkIV interferometer on board stratospheric research balloons. Infrared solar absorption spectra were acquired near 35° N latitude at altitudes between local tropopause and 38 km. Volume mixing ratio profiles of HF derived from 4 flights (1990-93) are in good qualitative agreement with time-dependent, two-dimensional model calculations and indicate an average rate of increase of 3.0 ± 0.4% per year.

INTRODUCTION

For almost a decade the importance of measurements of molecular concentration of stratospheric hydrofluoric acid (HF) has been emphasized for its distinctive role in the chemistry of halogenated gases and their effect in the depletion of stratospheric ozone [*McElroy and Salawitch*, 1989]. Gaseous HF in the Earth's stratosphere is believed to be entirely due to photodissociation of cholorofluorocarbons (CFC's). Therefore, the abundance of gaseous HF can be viewed as an indicator of the past rate of CFC's photolysis in the stratosphere. HF's primary path of destruction is its slow diffusion into the troposphere and eventual

1

rainout. Its stability in the atmosphere and its dominance in the stratospheric fluorine abundance was believed to prevent any catalytic reactions involving fluorine-species leading to ozone destruction [*Stolarski and Rundel,* 1975]. However, this could change as additional kinetic data of fluorine species containing CF_3 groups become available for evaluation of their impact on stratospheric ozone [*Ko et al.,* 1994]

INSTRUMENT AND BALLOON MEASUREMENTS

The JPL Michelson interferometer system (MkIV), built in 1985, has been operated on the ground, from aircraft, and from balloons. Solar absorption spectra covering the 600 - 5700 cm^{-1} spectral region are observed simultaneously using an InSb photodiode in parallel with a HgCdTe photoconductor. A more detailed description of the interferometer system for measuring atmospheric gases has been reported [*Toon,* 1991] and results of infrared measurements made from aircraft published [*Toon et al.,* 1992, 1989]. In this paper we present the analysis of solar absorption spectra, recorded by MkIV on board stratospheric balloons. Mid-latitude (35° N) column abundances of HF are reported along with volume mixing ratio (vmr) profiles.

Four sunset occultations were analyzed for this work. The three early flights were conducted from Ft. Sumner, NM, and the last flight was launched from Daggett, CA. Relevant flight parameters for these four balloon flights are summarized in Table 1. Pairs of spectra were averaged before being analyzed. Typically, 0.01 cm^{-1} interferograms were measured at solar zenith angles up to 93° (~28 km altitude), at which point we switched to 0.02 cm^{-1} to allow more rapid recording, and thereby prevent the tangent point separation of successive pairs of spectra from exceeding 3 km. Each analyzed spectrum therefore represents 100 or 200 seconds of observations.

DATA ANALYSIS

The JPL MkIV interferometer data analysis process consists of two separate procedures. Nonlinear least square (NLLS) fitting is first used to calculate the slant column abundance for each target gas in each spectrum. This is performed adjusting an initial guess of the vmr profile until the calculation best matches the observed spectrum. These slant columns, together with the matrix of geometrical

slant path distances, are then inverted using a linear equation solver subject to a second derivative constraint to yield vmr profiles [*Toon et al.* 1994.]

The molecular spectral parameters used in the spectral fitting calculation were taken from the ATMOS compilation [*Brown et al.*, 1987] but incorporating recent improvements from the HITRAN 92 linelist. To maximize the consistency of analysis and results, a single set of vmr profiles were used as an initial guess for all four balloon flights.

In addition to HF, spectral analyses and retrievals were performed on many other gases including CO_2, N_2O, and N_2. Solar zenith angles of individual spectra were determined by constraining retrieved mixing ratios of CO_2 to be consistent with *in-situ* measurements [*Schmidt and Khedim*, 1991]. This procedure was of particular importance for analysis of spectral data from the 1992 balloon flight where elevated concentrations of Pinatubo aerosols caused significant pointing anomalies in spectra recorded below 26 km altitude (and complete loss of sun below 22 km.) The pressure-temperature relation used in the spectral fitting algorithm was initially derived from radiosonde measurements compiled from stations around launch site and then refined using vmr profiles of CO_2 derived from temperature-sensitive lines in the MkIV spectra. The N_2 retrieval provided an independent diagnosis of the entire data analysis procedure and, since its vmr profile is well known, enabled an estimate of any residual systematic error. The importance of N_2O is that its long lifetime makes it an excellent tracer of atmospheric transport. Use of N_2O vmrs as a vertical ordinate therefore removes transport-induced disturbances and allows closer scrutiny of gaseous profiles than would otherwise be possible. It also enables meaningful comparison of disturbed measurements with 2-D (i.e. zonal) model predictions.

RESULTS AND DISCUSSION

Since its presence was first confirmed by *Zander et al.* [1977], stratospheric HF has been extensively studied because of its dominance in the stratospheric fluorine budget. Aircraft observations of stratospheric HF have previously been reported by *Toon et al.* [1992] from their analysis of solar spectra in the 4038.95 and 4109.94 cm^{-1} intervals. In addition, the HF line at 3877.70 cm^{-1} was included in this study. Errors associated with calculation of HF slant columns and vmr

profiles from MkIV spectra have been extensively discussed elsewhere [*Toon et al.*, 1994, 1989].

Figure 1 reproduces the measured mixing ratio profiles of HF and N_2O for the years 1990-93 (solid: 90; dotted: 91; dashed: 92; dashed-dotted: 93). The vertical coverage extends from the balloon down to the altitude where the limb path starts to become opaque. For compatibility with the forward model, the vertical separation of the retrieved vmr profiles was chosen to be 1 km, despite the tangent point spacing being 2-4 km typically. The figure clearly illustrates the considerable transport-induced variations between flights. That these variations are the result of transport, and not chemical changes in HF, is evident from careful scrutiny of the N_2O profiles, which are almost perfectly anti-correlated with those of HF. Consequently, plotting HF versus N_2O (figure 2) yields a very smooth and compact set of lines, the slight shifts arising from the secular increases of HF and N_2O.

The HF volume mixing ratio for the four flights at specific N_2O levels is summarized in Table 2. Also tabulated is an estimate of the annual linear increase in HF. The estimated small increase in stratospheric N_2O ($\sim0.5\%$/year) has been subtracted from the computed linear trend in HF. While the average increase in mid-stratosphere HF vmr of 3.0 ± 0.4%/year is consistent with estimations of total fluorine compound loading of the stratosphere [*Prinn*, 1988], our results show a clear increase with altitude. While other reports of long-term increases in HF [*Rinsland et al.*, 1991, Table 1] are 50 - 70% higher than those calculated here, most have been determined from measurements starting a decade or more earlier. When comparing HF increases deduced from measurements made at different times it must be noted that the annual growth in HF column is a declining percentage of the time dependent total burden. The linear increase computed in this study is in agreement with rates inferred from ground-based total column measurements made post 1987 [*Rinsland et al.*, 1991]. Also the increases in the budget of inorganic fluorine in the upper stratosphere inferred from ATMOS measurements made in 1985 and 1992 indicate an HF trend of 5.7 - 6% a year [*Zander et al.*, 1994], a value not inconsistent with MkIV observations at the highest altitudes. Despite the limited baseline of MkIV results, the trend nevertheless is

determined to high precision. This is directly attributable to the use of N_2O as the vertical ordinate removing dynamical variations.

MODEL COMPARISON

The two-dimensional (2D) model of stratospheric photochemistry and transport used in this study has been used previously in a number of stratospheric studies [*Jackman et al.,* 1990]. The model domain extends from the ground to approximately 90 km with a vertical grid equally spaced in log-pressure at $\sim$2 km intervals. The latitudinal extent is from 85° S to 85° N with a 10 degree spacing. Reaction rates and photodissociation cross sections from JPL-92 were used [*Demore et al.,* 1992]. The climatological temperature field is based on National Meteorological Center (NMC) data for the ground to 0.4 mb, and CIRA [1972] for levels above 0.4 mb. Heating rates and the residual circulation were calculated following *Rosenfield et al.,* [1987], and the horizontal eddy diffusion field (K_{yy}) was determined self-consistently from the residual circulation described elsewhere [*Fleming et al.,* 1994].

There are 27 transported species or families, including HF, $CFCl_3$, CF_2Cl_2, $CHClF_2$, $C_2Cl_3F_3$, $C_2Cl_2F_4$, C_2ClF_5, $CBrClF_2$, $CBrF_3$, $CClFO$, and CF_2O. Formation of inorganic fluorine is assumed to be due solely to the breakdown of CFC's. Details of the fluorine photochemistry contained in the model are described in a previous study of the stratospheric fluorine reservoir distributions [*Kaye et al.,* 1991]. Time dependent model calculations were carried out for the period 1970 - 2010, with source gas boundary conditions at the ground updated each year based on the scenarios described in detail in a recent international report [*WMO,* 1991].

The 2D model simulates the shape of the observed HF mixing ratio profile very well (figure 2), but always predicts more at altitudes above 20 km. The model rate of increase at the highest altitudes (5.6%) is in close agreement with observations but at lower altitudes the model over-predicts the rate of increase. A more thorough investigation of this model-observation difference is warranted but is beyond the scope of this paper. The qualitative agreement between the zonal mean model and MkIV measurement at an individual longitude illustrates the effectiveness with which N_2O mixing ratio profile can be used to eliminate local

5

transport effects. The compactness of the N_2O - HF relation indicates that the transport rates at any given stratospheric height is short compared to the local chemical lifetimes of both gases. The good agreement between observations and model calculation suggests that the overall chemistry of HF is well reproduced by the model.

COMPARISON WITH COLUMN MEASUREMENTS

For the purpose of comparing these results with recent ground-based measurements of HF, column abundances above 17.5 km were determined (Table 2). For the September 1992 flight, HF vmr profiles were extrapolated down to 17.5 km by assuming the same shape as in other years. Comparison of ground-based column values with ones determined from these balloon measurements are subject to error due to the lack of information below 17.5 km. While the content of HF below 17.5 km is expected to be small, it should be kept in mind that the column can vary considerably on a day to day basis due to atmospheric airmass origin [*Kaye et al.*, 1990]. This is demonstrated in figure 1 where the smaller HF vmrs in fall 1990 produced the pronounced minimum column value.

Ground-based solar spectra were acquired by MkIV one day prior to the balloon launch on all four years. The total HF columns derived from these spectra are summarized at the bottom of Table 2. They are in close agreement with the values determined from balloon measurements; a clear reflection of lack of significant HF below 17.5 km. The ratio of total HF column to that above 17.5 km (1.08 ± 0.04) is similar to that those published elsewhere [*Rinsland et al.*, 1991] and could provide estimates of non-stratospheric HF for purposes of observational and modeling exercises. Unfortunately any evaluation in the HF trend from column measurements are subject to large errors due to differing airmass origins, and seasonal changes in stratospheric conditions between observations. A long-term increase in derived from mixing ratio N_2O – HF scatter plots, however, avoids these uncertainties.

CONCLUSIONS

This study has primarily dealt with the determination of HF mixing ratio profiles in northern mid-latitudes. The main results confirm the continuing increase in stratospheric HF. The observed trend is largest at the highest measured altitudes

6

where it is in agreement with other measurements. The 2-D model calculations clearly demonstrate their ability to reproduce the HF chemistry but could benefit from the limits imposed on the rate of increase of stratospheric HF discussed in this study. The use of N_2O, in place of altitude or pressure, allows a more accurate comparison of HF mixing ratio profiles by eliminating the transport-induced variability inherent to sparse observations. Continued monitoring of HF is desirable to more accurately determine its continued growth and the rate of CFC photolysis in the stratosphere.

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Fig. 1. Mixing ratio profiles of N_2O (left panel) and HF (right panel) retrieved from MkIV measurements for years 1990 (solid line), 1991 (dotted line), 1992 (dashed line), and 1993 (dashed-dotted line). Symbols represent 1σ precision in retrieval.

Fig. 2. Mixing ratio scatter plots of measured N_2O and HF (symbols), with 1σ precision, and prediction from 2-D zonal model (solid line) for years 1990 through 1993 (panels left to right).

TABLE 1. MkIV Flight Parameters

	1990	1991	1992	1993
Date	27 Sept.	5 – 6 May	14 – 15 Sept.	4 Apr.
Launch Site	Ft. Sumner	Ft. Sumner	Ft. Sumner	Daggett
Tangent Lat. (°N)	34.2	37.5	35.2	34.8
Tangent Lon. (°E)	254	248.2	249.8	244.5
Balloon Alt. (km)	36	37	38	37
Min. Tangent Alt. (km)	10	16	22	17

TABLE 2

			HF (ppbv)		increase
Altitude	1990	1991	1992	1993	(%/year)

50 ppbv N_2O	0.76	0.84	0.86	0.90	4.1±1.0
100 ppbv N_2O	0.57	0.60	0.65	0.67	3.3±0.8
150 ppbv N_2O	0.44	0.46	0.48	0.51	2.0±0.6
200 ppbv N_2O	0.29	0.29	0.34	0.31	1.3±1.1
HF Column $(\times 10^{14}$ molec.cm$^{-2})$					
above 17.5 km	5.1±0.2	7.6±0.2	7.0±0.1	7.3±0.3	5.0±5.0
above ground	5.8±0.4	7.9±0.6	7.6±0.4	7.6±0.9	